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(54) Electrically conductive polymeric compositions.

(57) This invention relates to the injection moldable and extrusion type electrically conductive polymeric blend compositions preferably having a viscosity at 200°C at 0.73 sec⁻¹ of less than about 8×10^5 poises. The compositions used for elastomeric articles include a neutralised sulphonated polymer; graphite fibre at a concentration of 1 to 50 parts by weight per 100 parts by weight of neutralised sulphonated polymer; and a preferential plasticiser at less than 60 parts by weight based on 100 parts by weight of the neutralised sulphonated polymer. The compositions may also optionally include fillers, oils and other additives. These blend compositions can be readily processed due to their superior rheological properties on conventional plastic fabrication equipment, especially on low and high pressure injection molding or extrusion equipment into electrically conductive articles having excellent physical and electrical properties.

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1
2 It has been found surprisingly that polymeric blend
3 compositions formed from blends of neutralized sulfonated
4 elastomeric or thermoplastic polymers, in particular a select
5 class of neutralized sulfonated elastomeric or thermoplastic
6 polymers, carbon or graphite fiber having a defined fiber
7 length, and a preferential plasticizer have suitable rheo-
8 logical, physical, and electrical properties for the formation
9 of an electrically conductive polymeric article and are
10 readily reprocessable into complex shaped articles.

11
12 This present invention relates to
13 compositions of a neutralized sulfonated elastomer or
14 thermoplastic and carbon or graphite fiber having a defined
15 fiber length and preferential plasticizer, the result-
16 ant composition ^{preferably having} a viscosity at 0.73 sec^{-1} at 200°C. of
17 less than 8×10^5 poises. The compositions are readily pro-
18 cessable in a conventional injection molding process into a
19 high performance electrically conductive polymeric article
20 such as conductive fibers or conductive pads. The resultant
21 electrically conductive polymeric article has excellent physi-
22 cal properties such as tensile strength and compression set
23 and excellent electrical properties such as volume resist-
24 ivity. Various critically selected additives can be incor-
25 porated into the electrically conductive polymeric blend com-
26 positions such as certain specific fillers and certain speci-
27 fic oils or lubricants.

1 The neutralized sulfonated polymers of this present
2 invention are derived from unsaturated thermoplastic
3 or elastomeric polymers which include low unsaturated elas-
4 tomeric polymers such as Butyl rubber, and EPDM terpolymers
5 as well as other unsaturated elastomeric polymers such as
6 partially hydrogenated polyisoprenes, partially hydrogenated
7 polybutadienes, Neoprene, styrene-butadiene copolymers or
8 isoprene-styrene random copolymers and mixtures thereof. The
9 thermoplastic polymers of the present invention which are
10 sulfonated include generally polyvinyl aromatic and poly-
11 olefinic type thermoplastics.

12 The expression "Butyl rubber" as employed in the
13 specification and claims is intended to include copolymers
14 made from a polymerization reaction mixture having therein
15 from 70 to 99.5% by weight of an isoolefin which has
16 4 to 7 carbon atoms, e.g. isobutylene, and 0.5 to 30% by
17 weight of a conjugated multiolefin having from 4 to 14 carbon
18 atoms, e.g. isoprene. The resulting copolymer contains 85 to
19 99.8% by weight of combined isoolefin and 0.2 to 10% of com-
20 bined multiolefin, more preferably 1 to 4%, e.g. 2%. Butyl
21 rubber generally has a Staudinger molecular weight of 20,000
22 to 500,000, preferably 25,000 to 400,000, especially 100,000
23 to 400,000, and a Wijs Iodine No. of 0.5 to 50, preferably 1
24 to 15. The Mooney viscosity (ML, 1 + 8, 212°F.) of the Butyl
25 rubber is 5 to 90, more preferably 10 to 60, and most prefer-
26 ably 15 to 50. The preparation of Butyl rubber is described
27 in U.S. Patent 2,356,128 which is incorporated herein by refer-
28 ence. Illustrative of a useful Butyl rubber is Exxon Butyl
29 365 (Exxon Chemical Co.), having a mole percent unsaturation
30 of 2.0% and a Mooney viscosity (ML, 1 + 8, 212°F.) of 40-50.
31 Lower molecular weight Butyl rubbers can also be used, i.e.,
32 Butyl rubbers having a viscosity average molecular weight of
33 5,000 to 85,000 and a mole percent unsaturation of 1 to 5%
34 may be sulfonated to produce the polymers useful in this in-
35 vention. Preferably, these polymers have a viscosity average
36 molecular weight of 25,000 to 60,000.

The EPDM terpolymers are low unsaturated polymers having 1 to 10.0 wt. % olefinic unsaturation, more preferably 2 to 8, most preferably 3 to 7 defined according to the definition as found in ASTM-D-1418-64 and is intended to mean terpolymers containing ethylene and propylene in the backbone and a diene in the side chain. Illustrative methods for producing these terpolymers are found in U.S. Patent 3,280,082, British Patent 1,030,289 and French Patent 1,386,600. The preferred polymers contain 40 to 80 wt. % ethylene and 1 to 10 wt. % of a diene monomer, the balance of the polymer being propylene (10 to 53 wt. %). Preferably, the polymer contains 50 to 70 wt. % ethylene, e.g. 50 wt. % and 2.6 to 8.0 wt. % diene monomer, e.g. 5.0 wt. %. The diene monomer is preferably a nonconjugated diene. Illustrative of these nonconjugated diene monomers which may be used in the terpolymer (EPDM) are 1,4-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene and methyl tetrahydroindene. The EPDM terpolymers of this invention have a number average molecular weight (\bar{M}_n) as measured by GPC of 10,000 to 200,000, more preferably of 15,000 to 100,000. The Mooney viscosity (ML, 1 + 8, 212°F.) of the EPDM terpolymer is 5 to 90, more preferably 10 to 60, most preferably 15 to 50. The \bar{M}_v as measured by GPC of the EPDM terpolymer is preferably below 400,000 and more preferably below 300,000. The \bar{M}_w as measured by GPC of the EPDM terpolymer is preferably below 500,000 and more preferably below 400,000.

A typical useful EPDM is Vistalon 2504 (Exxon Chemical Co.), a terpolymer having a Mooney viscosity (ML, 1 + 8, 212°F.) of 40 and having an ethylene content of about 50 wt. % and a 5-ethylidene-2-norbornene content of about 5 wt. %. The \bar{M}_n of Vistalon 2504 as measured by GPC measurement is 100,000. The \bar{M}_v is 310,000 by GPC measurement and the \bar{M}_w is 360,000 by GPC measurement. Another EPDM terpolymer Vistalon 2504-20 is derived from V-2504 (Exxon Chemical Co.) by a controlled extrusion process, wherein the resultant Mooney

1 viscosity at 212°F. is 20. The \bar{M}_n of Vistalon 2504-20 is
2 90,000 by GPC measurement, the \bar{M}_v is 230,000 by GPC measure-
3 ment and the \bar{M}_w is 250,000 by GPC measurement. Nordel 1320
4 (DuPont) is another terpolymer having a Mooney viscosity of
5 212°F. of 25 and having 53 wt. % of ethylene, 3.5 wt. % of
6 1,4-hexadiene, and 43.5 wt. % of propylene.

7 The polyvinyl aromatic thermoplastic resins are
8 selected from the group consisting of polystyrene, poly-t-
9 butyl-styrene, polychlorostyrene, poly-methylstyrene and co-
10 or terpolymers of the aforementioned with acrylonitrile or
11 vinyl toluene and mixtures thereof. The polyvinylaromatic
12 based thermoplastics suitable for use in the practice of the
13 invention have a glass transition temperature from 80°C. to
14 150°C., more preferably 90°C. to 140°C. and most preferably
15 90°C. to 120°C. These polyvinylaromatic resins have a weight
16 average molecular weight (\bar{M}_n) as measured by GPC of 5,000 to
17 500,000, more preferably 20,000 to 350,000 and most preferably
18 90,000 to 300,000 wherein the polyvinylaromatic thermoplastic
19 resins can be prepared directly by any of the known polymeri-
20 zation processes. The number average molecular weight of
21 these polyvinyl aromatic thermoplastic resins is 5,000 to
22 2,000,000, more preferably 20,000 to 500,000. The term
23 "thermoplastic" is used in its conventional sense to mean a
24 substantially rigid (flexural modulus >10,000 psi) material
25 capable of retaining the ability of flow at elevated tempera-
26 tures for relatively long times. The preferred polyvinyl
27 aromatic thermoplastic resin is a homopolymer of styrene
28 having a number average molecular weight of 180,000, and an
29 intrinsic viscosity in toluene of 0.8. These polymers are
30 widely available commercially in large volume. A suitable
31 material is Dow Polystyrene 666 which has a number average
32 molecular weight of 230,000.

33 The polyolefinic thermoplastic resins of the present
34 invention include those which are based on the polymerization
35 of such monomers as ethylene, propylene, 4-methyl-1-pentene
36 and 1-butene. In order for these systems to be successfully

employed in the present invention, copolymers of such monomers with a suitable diene (e.g., 5-ethylidene-2-norbornene (ENB)) or an aromatic based olefin (e.g. styrene) must be employed. For example, crystalline copolymers of ethylene with ENB can be prepared in a manner identical to that employed to prepare ethylene-propylene terpolymers (EPDM), but with little or no propylene present. When such copolymers are prepared with diene contents less than 10%, they can be highly crystalline and behave as thermoplastics. Despite the fact that these systems will always require some diene present, we shall refer to these materials as polyolefins. The same types of crystalline systems can be prepared with propylene/diene, butene-1/diene, etc. In all cases these polymers are rigid plastic systems which can be sulfonated by the techniques described below.

In carrying out the sulfonation the polymer is dissolved in a non-reactive solvent or formed in situ in the non-reactive solvent such as a chlorinated aliphatic hydrocarbon, chlorinated aromatic hydrocarbon, an aromatic hydrocarbon, or an aliphatic chlorinated hydrocarbon such as carbon tetrachloride, dichloroethane, chlorobenzene, benzene, toluene, xylene, cyclohexane, pentane, isopentane, hexane, isohexane or heptane. The preferred solvents for elastomeric polymers are the lower boiling aliphatic hydrocarbons and the preferred solvent for the thermoplastic polymers is dichloroethane. A sulfonating agent is added to the solution (cement) of the polymer and non-reactive solvent at a temperature of -100°C . to 100°C . for a period of time sufficient to effect sulfonation, for example 1 to 60 minutes, most preferably at room temperature for 5 to 45 minutes; and most preferably 10 to 30. Typical sulfonating agents are described in U.S. Patents 3,642,728 and 3,836,511. These sulfonating agents are selected from an acyl sulfate, a mixture of sulfuric acid and an acid anhydride or a complex of a sulfur trioxide donor and a Lewis base containing oxygen, sulfur, or phosphorus. Typical sulfur trioxide donors are SO_3 , chlorosulfonic acid, fluorosulfonic

1 acid, sulfuric acid, oleum, etc. Typical Lewis bases are:
2 dioxane, tetrahydrofuran, tetrahydrothiophenol or triethyl-
3 phosphate. The most preferred sulfonation agent for the
4 sulfonation process is an acyl sulfate selected from the
5 group consisting of benzoyl, acetyl, propionyl or butyryl
6 sulfate. The acyl sulfate can be formed in situ in the re-
7 action medium or pregenerated before its addition to the
8 reaction medium in a chlorinated aliphatic or aromatic hydro-
9 carbon. It should be pointed out that neither the sulfonating
10 agent nor the manner of sulfonation is critical, provided that
11 the sulfonating method does not degrade the polymeric backbone

12 The sulfonation reaction is quenched by the addition
13 of an aliphatic alcohol to the cement. Suitable examples of
14 quenching agents are methanol, ethanol, isopropanol, an aro-
15 matic hydroxyl compound, such as phenol, a cycloaliphatic
16 alcohol such as cyclohexanol or water. The sulfonated polymer
17 of the sulfonated elastomeric polymer has 5 to 100
18 meq. sulfonate groups per 100 grams of sulfonated polymer,
19 more preferably 10 to 50, and most preferably
20 15 to 40. The meq. of sulfonate groups/100 grams of
21 polymer is determined by both titration of the sulfonated
22 polymer and Dietert Sulfur analysis. In the titration of the
23 sulfonated polymer, the polymer is dissolved in solvent con-
24 sisting of 95 parts of toluene and 5 parts of methanol at a
25 concentration level of 50 grams per liter of solvent. The
26 sulfonated polymer is titrated with ethanolic sodium hydroxide
27 to an Alizarin Thymolphthalein endpoint.

28 The sulfonated polymer substantially is gel-free
29 and hydrolytically stable. Gel is measured by stirring a
30 given weight of sulfonated polymer in a solvent comprised of
31 95 toluene-5-methanol at a concentration of 5 wt. % polymer
32 for 24 hours, allowing the mixture to settle, withdrawing a
33 weighed sample of the supernatant solution and evaporating
34 to dryness. Hydrolytically stable means that the sulfonated
35 polymer will not be eliminated under neutral or slightly basic

conditions to a neutral moiety which is incapable of being converted to highly ionic functionality.

Neutralization of the sulfonated polymer is by the addition of a solution of a basic material to the unneutralized sulfonated polymer dissolved in the mixture of the aliphatic alcohol and non-reactive solvent. The basic material such as a basic salt is dissolved in a binary solvent system consisting of water and/or an aliphatic alcohol. The counterion of the basic salt is selected from the group consisting of antimony, ammonium, aluminum, lead and metal ions from Group IA, IIA, IB and IIB of the Periodic Table of Elements and mixtures thereof. The anion of the basic salt is selected from the group consisting of a carboxylic acid having from 1 to 22 carbon atoms, more preferably 2 to 4 carbon atoms, a hydroxide and alkoxide having about 1 to 4 carbon atoms and mixtures thereof. The preferred neutralizing agent is a metal acetate, more preferably zinc acetate. Sufficient basic salt of the carboxylic acid is added to the solution of the sulfonated polymer to effect neutralization. It is preferable to neutralize at least 95% of the sulfonated polymer, more preferably 98%, most preferably 100%. Other basic materials useful for neutralization are metal oxides such as MgO, CaO, BaO, ZnO, Ag₂O, PbO₂ and Pb₃O₄. Metal hydroxides are also useful as neutralizing agents such as NaOH, KOH, LiOH, Mg(OH)₂ and Ba(OH)₂. Alternatively, but less preferred, organic amines as described in U.S. Patent 3,642,728, can be used to neutralize the sulfonated polymer. The resultant neutralized sulfonated polymer has a melt viscosity at 0.73 sec⁻¹ at 200°C., of 1×10^4 to 8×10^5 poises, more preferably 2×10^4 to 5×10^5 poises and most preferably 3×10^4 to 3×10^5 poises.

A means of characterizing the apparent molecular weight of a polymer involves the use of melt rheological measurements. For ionic polymers, this is the preferred method since solution techniques are difficult to interpret due to the complex nature of the ionic associations. Melt

1 rheological measurements of apparent viscosity at a controlled
2 temperature and shear rate can be used as a measure of apparent
3 molecular weight of an ionic polymer. Although the exact re-
4 lationship between melt viscosity and apparent molecular
5 weight for these ionic systems is not known, for the purposes
6 of this invention the relationship will be assumed to be one
7 of direct proportionality. Thus, in comparing two materials,
8 the one with the higher melt viscosity will be associated with
9 the higher apparent molecular weight (which includes the de-
10 gree of ionic association). The melt viscosity of the systems
11 investigated were determined by the use of an Instron Capillary
12 Rheometer. Generally, the melt viscosity measurements were
13 made at a temperature of 200°C. and at various shear rates
14 corresponding to crosshead speeds from .005 in/min to 20
15 in/min and a capillary die of 0.05 in diameter. The
16 apparent viscosity at 200°C and at a shear rate of .73 sec⁻¹
17 (.005 in/min) is employed as a characterization parameter
18 in this invention. A measure of the melt elasticity of a
19 given system can also be obtained from these rheological
20 measurements. A type of flow instability known as melt
21 fracture is exhibited by many polymeric materials having high
22 molecular weight. This phenomenon is shear sensitive and
23 thus will generally exhibit itself at a given shear rate and
24 temperature. The shear rate for the onset of melt fracture
25 indicates the upper shear rate for processing a given material.
26 This is used as a characterization parameter for compounds
27 employed in extrusion processing.

28 The metal or ammonium neutralized sulfonate contain-
29 ing polymers at the higher sulfonate levels possess extremely
30 high melt viscosities and are thereby difficult to process.
31 The addition of ionic group plasticizers markedly reduces melt
32 viscosity and frequently enhances physical properties. To
33 the neutralized sulfonated polymer is added, in either solu-
34 tion or the crumb of the neutralized sulfonated polymer, a
35 preferential plasticizer selected from

1 aliphatic carboxylic acid having 5 to 30 carbon
2 atoms, more preferably 8 to 22 carbon atoms/^{per molecule} and
3 basic salts of these aliphatic carboxylic acids, wherein the
4 metal ion of the basic salt is aluminum, iron, antimony, lead, a
5 metal ion from Groups IA, IIA, IB or IIB of the Periodic
6 Table of Elements or a mixture thereof. The preferred car-
7 boxylic acid salts are formed from lauric, myristic, palmitic
8 and stearic acids or a mixture thereof; e.g. zinc stearate,
9 magnesium stearate, or zinc laurate. The preferred preferen-
10 tial plasticizers are the metallic salts of the aliphatic
11 carboxylic acids.

12 The preferential plasticizer is incorporated into
13 the neutralized sulfonated polymer at 3 to 60 parts by
14 weight based on 100 parts by weight of the neutralized
15 sulfonated polymer, more preferably at 9 to 40 and
16 most preferably at 10 to 25/^{parts by weight/100 parts by weight} of polymer.
17 salt of the aliphatic carboxylic acid can also be used as
18 neutralizing agent. In the case of the neutralizing agent and
19 plasticizer being the identical chemical species, additional
20 metallic salt is added over the required levels of neutraliza-
21 tion. Alternatively, other preferential plasticizers are
22 selected from ureas, thioureas and amides such as stearamide,
23 and mixtures thereof. The preferred plasticizers are selected
24 from the metallic salts of the aliphatic carboxylic acids.
25 Materials such as alcohols, esters, ethers or ketones are not
26 suitable plasticizers for the present invention. The resultant
27 neutralized sulfonated polymer with preferential plasticizer
28 is isolated from the solution by conventional steam stripping
29 and filtration.

30 The neutralized sulfonated polymer is blended with
31 the graphite fiber having a fiber length of less than 1 inch
32 by techniques well known in the art. For example, the blend
33 composition can be compounded on a two-roll mill. Other
34 methods known in the art which are suitable for making these
35

1 compositions include those methods employed in the plastic
2 and elastomer industries for mixing polymer systems. An
3 excellent polymeric blend composition of this invention can be
4 obtained through the use of a high shear batch intensive mixer
5 called the Banbury. Alternatively, economic advantages in
6 terms of time and labor savings can be obtained through the
7 use of a Farrel Continuous Mixer (FCM), a twin screw extruder,
8 or tandem extrusion techniques which are continuous mixing
9 types of equipment. The Banbury mixing device is the pre-
10 ferred batch type mixer, and the twin screw extruder or FCM
11 is the preferred continuous mixer.

12 The graphite fibers can be
13 generally defined as carbon or graphitized carbon filaments
14 derived, for example, from spun fibers of poly(acrylonitrile),
15 rayon or petroleum pitch. The fibers used in the examples of
16 the present invention have a diameter of 8 μ m to 15 μ m and
17 lengths of 0.125 to 1.0 inches, a tensile modulus of 1×10^7
18 to 5×10^7 psi and a tensile strength of 100,000 to 500,000
19 psi.

20 The graphite fibers are incorporated into the blend
21 composition at a concentration level of 1 to 50 parts by
22 weight per 100 parts by weight of the neutralized sulfonated
23 polymer, more preferably at 5 to 35, and most preferably at
24 10 to 20.

25 Oils and fillers can be optionally added to the
26 polymeric blend composition to modify the physical properties
27 of these compositions. The oils which can be optionally em-
28 ployed in the present invention are non-polar process oils
29 having less than 2 wt. % polar type compounds as measured by
30 molecular type clay gel analysis. These oils are selected
31 from paraffinics ASTM Type 104B oils, as defined in ASTM-D-
32 2226-70, aromatics ASTM Type 102 oils or naphthenics ASTM
33 Type 104A oils, wherein the oil has a flash point by the
34 Cleveland open cup of at least 350°F., a pour point of less
35 than 40°F., a viscosity of 70 to 3000 ssu's at 100°F. and a

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1 number average molecular as measured by GPC of 300 to 1000.
2 and more preferably 300 to 750. The preferred process oils
3 are paraffinic oils. Table I illustrates typical oils en-
4 compassed by the scope of this invention. The oils are in-
5 corporated into the blend composition at a concentration
6 level of 5 to 150 parts by weight based on 100 parts by
7 weight of the neutralized sulfonated polymer, more preferably
8 at 25 to 100, and most preferably at 40 to 100.

TABLE I

1	2	3	4	5	6	7	8	9	10
	Type Oil	Oil Code No	Viscosity ssu	Mn	% Polars	% Aromatic	% Saturates		
4	Paraffinic	Sunpar 115	155	400	0.3	12.7	87.0		
5	Paraffinic	Sunpar 180	750	570	0.7	17.0	82.3		
6	Paraffinic	Sunpar 2280	2907	720	1.5	22.0	76.5		
7	Aromatic	Flexon 340	120	-	1.3	70.3	28.4		
8	Naphthenic	Flexon 765	505	-	0.9	20.8	78.3		
9	Paraffinic	Tufflo 6056	495	-	0.0	0.9	99.1		
10	Naphthenic	Tufflo 6054	580	-	0.0	8.0	92.0		

1 The fillers optionally employed in the present
2 invention are selected from the group consisting of carbon
3 blacks, talcs, ground calcium carbonate, water precipitated
4 calcium carbonate, delaminated, calcined and hydrated clays
5 and amorphous silica and mixtures thereof. Examples of carbon
6 black are the furnace, channel or thermal blacks. These fill-
7 lers are incorporated into the blend composition at 1 to 300
8 parts by weight based on 100 parts by weight of the neutral-
9 ized sulfonated polymer, more preferably at 5 to 250; and
10 most preferably at 10 to 200 parts.

11 Various other additives can be optionally incorpor-
12 ated into the polymeric blend compositions to improve the
13 physical properties, the appearance, the chemical properties
14 of the formed elastomeric article or to modify the processa-
15 bility of the blend compositions. Zinc oxide can be incor-
16 porated into the blend as a means for improving the ionic
17 bonding force between the sulfonate groups in the sulfonated
18 polymer. The zinc oxide is incorporated into the blend com-
19 position at a concentration level of less than 25 parts
20 by weight based on 100 parts by weight of the neutralized
21 sulfonated polymer, more preferably at less than 15.

22 A metallic hydroxide can be incorporated into the
23 blend composition as a means of further neutralizing any
24 unneutralized sulfonate groups in the compositions. The
25 metallic hydroxide is incorporated at a concentration level
26 of less than 50 parts by weight per hundred based on
27 100 parts by weight of the neutralized sulfonated polymer,
28 wherein the metal ion of the metallic hydroxide is selected
29 from Group IIA of the Periodic Table of Elements such as
30 barium, calcium and magnesium.

31 A lubricant can be employed in the blend composi-
32 tion at a concentration level of 1 to 20 parts
33 by weight based on 100 parts by weight of the neutralized
34 sulfonated polymers, and more preferably 1 to 15.
35 The lubricants of the present instant invention are non-polar
36 paraffinic hydrocarbon waxes having a softening point of

1 125°F. to 220°F., more preferably 150°F. to 200°F., wherein
2 the wax has a number average molecular weight as measured by
3 GPC of 1000 to 4000, more preferably 1500 to 3500, and less
4 than 2 wt. % polar constituents. These lubricants modify
5 the rheological properties of the composition, improve the
6 processability in forming the polymeric article and impart
7 a shine or gloss to the polymeric article. Additionally,
8 amorphous polypropylene can be used as a lubricant.

9
10 The advantages of both the electrical and physical
11 properties of the polymeric blend compositions of the present
12 invention can be more readily appreciated by reference to the
13 following example

14 EXAMPLE

15 Graphite fiber/zinc neutralized, sulfonated polymer
16 compositions were prepared by blending the fibers in a solu-
17 tion of the polymer in a mixed solvent of 90% hexane and 5%
18 isopropanol followed by evaporation of the solvent and drying
19 of the compound. The compositions prepared are described in
20 Table I. The graphite fibers were a commercial product based
21 on a poly(acrylonitrile) precursor and were nominally 8 μ m in
22 diameter and 1/8 inch in length. The polymer was a zinc
23 neutralized, sulfonated EPDM rubber containing 56 percent
24 ethylene and 30 mmoles sulfonate per 100 grams polymer.

25 Rectangular samples of various lengths were pre-
26 pared by compression molding the compositions. The electrical
27 resistances across the length of the samples were measured
28 with a volt-ohm meter and the resistivity was determined by
29 multiplying the resistance by the cross-sectional area and
30 dividing by the length of the specimen. These data are given
31 in Table III. The low resistivities clearly demonstrate that
32 these materials are conductive. The mechanical properties
33 of the compounds are given in Table IV and demonstrate the
34 reinforcing effect the fibers have on the polymer.

TABLE II

Sample	Parts by Weight		
	Polymer	Graphite Fibers	Zinc Stearate
5342-117 A	100	11	10
5342-117 B	100	25	10
5342-117 C	100	43	10

TABLE III

Sample	Fiber Concentration, wt. %	Sample Length in.	Gross Sectional Area, in ²	Resistance ohms	Resistance with ohms-in
5342-117 A	10	1	0.24	2	0.5
5342-117 A	10	2	0.24	3.5	0.4
5342-117 A	10	3	0.24	4	0.3
5342-117 A	10	4	0.24	5	0.3
5342-117 A	10	5	0.24	6	0.3
5342-117 A	10	6	0.24	10	0.4
5342-117 B	25	1	0.34	0.5	0.1
5342-117 B	25	2	0.34	0.8	0.1
5342-117 B	25	3	0.34	1.0	0.1
5342-117 B	25	4	0.34	1.2	0.1
5342-117 B	25	5	0.34	1.4	0.1
5342-117 B	25	6	0.34	2	0.1
5342-117 C	40	1	0.34	0.4	0.1
5342-117 C	40	2	0.34	0.5	0.09
5342-117 C	40	3	0.34	0.5	0.06
5342-117 C	40	4	0.34	0.8	0.07
5342-117 C	40	5	0.34	0.9	0.06
5342-117 C	40	6	0.34	1.2	0.07

TABLE IV

Sample	Fiber Concentration (wt. %)	Tensile Modulus (psi)	Tensile Strength (psi)
5342-117 A	10	1.6×10^5	2200
5342-117 B	25	2.2×10^5	2900
5342-117 C	40	4.7×10^5	4500

WHAT WE CLAIM IS:

1. A polymeric composition which comprises:

(a) a neutralised sulphonated polymer having 5 to 100 meq. neutralised sulphonate groups per 100 grams of said neutralised sulphonated polymer;

(b) 1 to 50 parts by weight of a carbon or graphite fibre per 100 parts by weight of said neutralised sulphonated polymer; and

(c) at least 3 parts by weight of a preferential ionic plasticiser based on 100 parts by weight of said neutralised polymer.

2. A composition according to claim 1, wherein said neutralised sulphonated polymer is formed from an elastomeric polymer which is a copolymer of an isoolefin and a conjugated multiolefin or an EPDM terpolymer.

3. A composition according to claim 1, wherein said neutralised sulphonated polymer is formed from a polyvinyl aromatic thermoplastic.

4. A composition according to claim 3 wherein the polyvinyl aromatic thermoplastic comprises polystyrene, poly-t-butyl styrene, polychlorostyrene, poly-methylstyrene, a terpolymer of the aforementioned with acrylonitrile or vinyl toluene or a mixture thereof.

5. A composition according to any one of the preceding claims wherein said neutralised sulphonate groups are neutralised with a counterion which is ammonium, antimony, aluminum, lead or a metal ion from Groups IA, IIA, IB or IIB of the Periodic Table of Elements or a mixture thereof.

6. A composition according to any one of the preceding claims wherein the amount of preferential plasticiser is at least 9 parts by weight based on 100 parts by weight of said neutralised sulphonated polymer.

7. A composition according to any one of the preceding claims, wherein said preferential plasticiser comprises a carboxylic acid, a metallic salt of a carboxylic acid or a mixture thereof, said carboxylic acid having 5 to 30 carbon atoms per molecule.
8. The composition according to claim 7, wherein said preferential plasticiser is zinc stearate.
9. A composition according to any one of claims 1 to 6 wherein said preferential plasticiser is a combination of stearic acid and a metal salt of said stearic acid, said metal being lead, antimony, aluminium or a metal from Groups IA, IIA, IB or IIB of the Periodic Table of Elements or a mixture thereof.
10. A composition according to any one of claims 1 to 6, wherein said preferential plasticiser comprises an amide, an urea, a thiourea or a metallic salt of an aliphatic carboxylic acid having 5 to 10 carbon atoms per molecule.
11. A composition according to any one of the preceding claims, wherein said graphite fibre has a fibre length of 0.01 inches to 1.0 inches.
12. A composition according to any one of the preceding claims, which includes a non-polar process oil comprising a paraffinic oil, a naphthenic oil, an aromatic oil, a mixture thereof or a crystalline hydrocarbon having a melting point of 135°F to 220°F and a \bar{M}_n of 1000 to 4000, or a filler comprising carbon black, calcium carbonate, amorphous silica, talc, clay or a mixture thereof; or a mixture of said oil and said filler, wherein said filler is carbon black, calcium carbonate, amorphous silica, talc, clay or a mixture thereof.

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			APPLICATION NO.
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 4 118 353</u> (S. MAKOWSKI et al.) * Claims 1-6; column 8, lines 36-57 * --	1	H 01 B 1/24
A	<u>US - A - 4 127 546</u> (D. LUNDBERG et al.) * Claims 1,22; column 10, lines 23-34 * --	1	
A	<u>DE - A - 2 723 339</u> (E.I. DU PONT DE NEMOURS) * Claim 1 * --	1	TECHNICAL FIELDS SEARCHED (Int.Cl.) H 01 B 1/24 C 08 L 23/32 H 01 B 3/00 C 08 L 25/18 41/00 C 08 K 7/06
A	<u>GB - A - 2 002 782</u> (AGENCY OF INDUSTRIAL SCIENCE & TECHNOLOGY) * Claim 1 * ----	1	
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X The present search report has been drawn up for all claims			& member of the same patent family. corresponding document?
Place of search The Hague		Date of completion of the search 02-07-1980	Examiner V.D. BULCKE